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(54) Title: TRIMERISING AND OLIGOMERISING OLEFINS USING A CHROMIUM BASED CATALYST

(57) Abstract: A trimerisation catalyst system includes a chromium source and a ligand comprising a substituted five membered carbocyclic ring or derivatives thereof. The five membered carbocyclic ring may be a substituted cyclopentadiene derivative of the general formula, C<sub>5</sub>R<sub>n</sub>H<sub>6-n</sub>, wherein each R is a substituent and n is an integer from 1 to 5.



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## TRIMERISING AND OLIGOMERISING OLEFINS USING A CHROMIUM BASED CATALYST

### 5 FIELD OF THE INVENTION

This invention relates to a hydrocarbon conversion catalyst system and the use thereof in a hydrocarbon conversion process, such as the oligomerisation or trimerisation of olefins, for example, ethylene.

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### BACKGROUND OF THE INVENTION

The oligomerisation of olefins, primarily  $\alpha$ -olefins, with chromium catalysts has been extensively studied. More specifically, a number of chromium catalysts  
15 have been developed and used to trimerise olefins. In this regard, the trimerisation of ethylene to 1-hexene is significant since, in addition to its use as a specific chemical, 1-hexene is extensively used in polymerization processes either as a monomer or co-monomer. Furthermore, the trimeric products derived from longer chain olefins could be well utilized as synthetic  
20 lubricants (e.g. polyalphaolefins / PAOs), as well as various other applications such as components of drilling muds, and as feedstock to prepare detergents and plasticizers.

Known chromium-based processes for the trimerisation of ethylene to 1-  
25 hexene include:

- a) A process in which olefins are trimerised by passing the olefin in contact with a catalyst comprising the reaction product of a chromium compound, an organoaluminium compound hydrolyzed with a specific amount of water  
30 and a donor ligand selected from hydrocarbyl isonitriles, amines and ethers (US Patent No. 4,668,838);

- b) Trimerisation of olefins by chromium-containing compounds, such as, for example, chromium pyrrolides that are prepared by forming a mixture of a chromium salt, a metal amide and an electron pair donor solvent, such as, for example, an ether. These chromium catalysts can be used either unsupported or supported on an inorganic oxide (European Patent No. 0 416 304);
- c) A process for oligomerising ethylene to produce 1-butene and/or 1-hexene wherein catalytic composition is obtained by mixing at least one chromium compound with at least one aryloxy aluminium compound with general formula  $R_nAl(R'O)_{3-n}$  where R is a linear or branched hydrocarbyl radical containing 1 to 30 carbon atoms, R'O is an aryloxy radical containing 6 to 80 carbon atoms and  $n$  is a whole which can take the values 0, 1 or 2, and with at least one other hydrocarbyl aluminium compound selected from tris(hydrocarbyl)aluminium compound or chlorinated or brominated hydrocarbyl aluminium compounds (US Patent No. 6,031,145);
- d) A process for producing 1-hexene which comprises trimerising ethylene in a 1-hexene solvent in the presence of a catalyst system obtainable by contacting in a 1-hexene solvent a chromium-containing compound, trialkylaluminium or dialkylaluminium hydride, a pyrrole compound or derivative thereof and a group 13 (III B) or group 14 (IV B) halogen compound (European Patent No. 0 699 648);
- e) A process for the trimerisation of ethylene, said process comprising reacting ethylene, using a catalyst comprising an aluminoxane and a polydentate phosphine, arsenic and/or antimony coordination complex of a chromium salt, such that 1-hexene is formed (US Patent No. 5,811,618).
- f) A process for the trimerisation of olefins comprising contacting a monomeric olefin or mixture of olefins under trimerisation conditions with a catalyst which comprises a source of chromium, molybdenum or tungsten; a ligand containing at least one phosphorous, arsenic or antimony atom bound to at least one hydrocarbyl group having a polar substituent, but

excluding the case where all such polar substituents are phosphane, arsane or stibane groups; and optionally an activator (WO Patent No. 02/04119)

5 Many of the known chromium-based processes for the trimerisation of ethylene are centred around catalyst systems that contain a pyrrole ligand in order to achieve the required selectivity and activity towards the formation of the desired products. As the pyrrole source, any pyrrole derivative containing a NH functionality is used as a ligand in the reaction.

10

The prior art catalyst systems and processes suffer from various drawbacks, including but not limited to, the need for using a pyrrole or related heteroaromatic analogues to achieve the required selectivity towards the formation of the desired products.

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## **SUMMARY OF THE INVENTION**

This invention recognizes the need for a catalyst system, which eliminates the need for using a pyrrole or related heteroaromatic analogues to achieve the  
20 required selectivity towards the formation of the desired products.

Thus, according to a first aspect of the invention, there is provided a trimerisation catalyst system, which includes a chromium source and a ligand comprising a substituted five membered carbocyclic ring or derivatives  
25 thereof.

30

The five membered carbocyclic ring may be a substituted cyclopentadiene derivative of the general formula,  $C_5R_nH_{6-n}$ , wherein each R is a substituent and n is an integer from 1 to 5.

The catalyst system may include a combination of at least a chromium source, a metal alkyl, a halogen source, and a substituted cyclopentadiene ligand.

The catalyst system of the invention attempts to address the need for using a pyrrole or related heteroaromatic analogues to achieve the required selectivity towards the formation of the desired products without compromising the advantages associated with the known homogeneous systems.

5

According to a second aspect of the invention there is provided a process by which 1-hexene can be produced in a high selectivity and yield by the trimerisation of ethylene under trimerisation conditions of temperature and pressure in the presence of an ethylene trimerisation catalyst system comprising a combination of at least a chromium source, a metal alkyl, a

10

halogen source and a substituted cyclopentadiene ligand.

The process may be carried out at pressures from 5 to 80 barg.

15

The process may be carried out at temperatures from 25 °C to 150 °C.

The chromium source of said catalyst system may consist of one or more organic and/or inorganic chromium compounds, with the chromium oxidation state ranging from 0 to 6.

20

The chromium compounds may suitably be expressed by the general formula  $\text{CrX}_n$ , wherein X can be the same or different and represents an organic or inorganic radical, group or compound, and n is an integer from 0 to 6.

25

Typical organic radicals may have from about 1 to 20 carbon atoms per radical, and are selected from the group consisting of alkyl, alkoxy, ester, ketone and/or amido radicals.

30

Typical organic compounds include, but are not limited to an amine compound, a phosphine compound, a phosphine oxide compound, a nitrosyl group and/or an ether compound.

Examples of the inorganic radicals may include halides, nitrates and sulfates.

Specific examples of chromium sources may include chromium(III)acetylacetonate, chromium (III) acetate, chromium (III) pyrrolides, chromium (III) 2,2,6,6-tetramethylheptadionate, chromium (III) tris(2-ethylhexanoate), bis(*N,N'*-bis(trimethylsilyl)benzamidinato) chromium (III) chloride, trichlorotris(4-isopropylpyridine) chromium (III), trichloro (*N,N,N',N',N''*-pentamethyldiethylenetriamine) chromium (III), chromium (III) chloride, bis-(2-dimethylphosphino-ethyl)ethylphosphine chromium (III), (2-dimethylphosphino-ethyl)(3-dimethylphosphinopropyl)methylphosphine chromium (III) chromium (III) naphthenate, chromium (II) acetate, chromium (II) pyrrolides, chromium (II) bis(2-ethylhexanoate) and/or chromium (II) chloride.

According to a third aspect of the invention, there is provided a ligand for an trimerisation catalyst system which includes a chromium source, the ligand comprising a substituted five membered carbocyclic ring or derivatives thereof.

The ligand may be a substituted cyclopentadiene derivative of the general formula,  $C_5R_nH_{6-n}$ , wherein each R is a substituent and n is an integer from 0 to 5.

The substituents may independently be selected from the group consisting of alkyl, aryl, aryloxy, halogen, nitro, alkoxycarbonyl, carbonyloxy, alkoxy, silyl, aminocarbonyl, carbonylamino, dialkylamino, or derivatives thereof, or aryl substituted with any of these substituents.

Typically the aryl group is a phenyl group and n is an integer from 0 to 5.

Specific examples of cyclopentadiene ligands may include 1,2,3,4-tetraphenylcyclopenta-1,3-diene, 1,2,3,4,5-pentaphenylcyclopenta-1,3-diene, 1,2,3,4,5-pentabenzylcyclopenta-1,3-diene, 5-methyl-1,2,3,4-tetraphenylcyclopenta-1,3-diene, 1,3-diphenylcyclopenta-1,3-diene, 1-phenyl-2,3,4,5-tetrapropylcyclopenta-1,3-diene, 1,4,5-triphenylcyclopenta-1,3-diene,

1,2,3,4-tetraphenyl-1,3-cyclopentadienyl-dimethyl-*t*-butylsilane, 5-benzyl-  
 1,2,3,4-tetraphenylcyclopenta-1,3-diene, 1,2,3,4-tetraphenyl-5-*p*-  
 tolylcyclopenta-1,3-diene, 5-mesityl-1,2,3,4-tetraphenylcyclopenta-1,3-diene,  
 5-(4'-*t*-butylphenyl)-1,2,3,4-tetraphenylcyclopenta-1,3-diene, 5-(4'-  
 5 chlorophenyl)-1,2,3,4-tetraphenylcyclopenta-1,3-diene, 5-(4'-fluorophenyl)-  
 1,2,3,4-tetraphenylcyclopenta-1,3-diene, 5-(pentafluorophenyl)-1,2,3,4-  
 tetraphenylcyclopenta-1,3-diene, 1,2,3,4-tetraphenyl-5-(phenylethynyl)  
 cyclopenta-1,3-diene, 2,3,4,5-tetraphenyl-2,4-cyclopentadienol, (1,3)(1,4)-di-*t*-  
 butylcyclopenta-1,3-diene, 1,3-di-*t*-butyl-cyclopentadienyltrimethylsilane,  
 10 pentakis(4'-*t*-butylphenyl) cyclopenta-1,3-diene and/ or derivatives thereof.

The term "cyclopentadiene" refers to a compound containing a 5-membered,  
 carbocycle. Derivatives of cyclopentadiene may include substituted  
 cyclopentadienes and/or any heteroleptic or homoleptic metal  
 15 cyclopentadienyl complexes or salts.

The cyclopentadiene containing ligand may be either affirmatively added to  
 the catalyst system, to the reaction mixture, or generated in-situ.

20 Examples of cyclopentadiene-containing compounds suitable to form or  
 generate ligands include, but are not limited to 1,2,3,4,5-  
 pentaphenylcyclopentadiene, lithium 1,2,3,4,5-pentaphenylcyclopentadienide,  
 diethyl-aluminium-1,2,3,4,5-pentaphenylcyclopentadienide, 1,3-  
 diphenylcyclopentadiene, lithium 1,3-diphenylcyclopentadienide,  
 25 diethylaluminium-1,3-diphenylcyclopentadienide, 1,2,3,4-  
 tetraphenylcyclopentadiene, lithium 1,2,3,4-tetraphenylcyclopentadienide,  
 diethyl-aluminium-1,2,3,4-tetraphenylcyclopentadienide or derivatives thereof  
 or the like.

30 A metal alkyl may also be present in the catalyst system.

The metal alkyl may be any heteroleptic or homoleptic metal alkyl compound.  
 One or more metal alkyls can be used.

Typically the alkyl ligand(s) is any saturated aliphatic radical. The alkyl ligand(s) on the metal may be aliphatic or aromatic. The metal alkyl may have any number of carbon atoms, but typically less than about 20 carbon atoms per molecule.

5

Examples of the afore-mentioned metal alkyl compounds include, but are not limited to, alkyl aluminium compounds, hydrolyzed alkyl aluminium compounds (aluminoxanes), alkyl boron compounds, alkyl magnesium compounds, alkyl zinc compounds and/or alkyl lithium compounds.

10 Preferably, the metal alkyl is an alkyl aluminium compound, hydrolyzed alkyl aluminium compound and/or alkyl boron compound.

Typically the metal alkyl is an alkyl aluminium compound, expressed by the following formulae:  $AlX_nR_{3-n}$  and  $R_nAlOR_{3-n}$ , wherein  $n$  is an integer,  $R$  is an alkyl group and  $X$  is a halogen atom.

15

The use of said alkyl aluminium compound is advantageous to activity.

Specific alkyl aluminium compounds may include trimethyl aluminium, triethyl aluminium, tripropyl aluminium, tributyl aluminium, triisobutyl aluminium, diethyl aluminium chloride, diethyl aluminium bromide, diethyl aluminium ethoxide, ethyl aluminium dichloride, ethyl aluminium sesquichloride, or the like, and mixtures thereof.

20

25 A halogen source may also be present in the catalyst system.

The halogen source may be any organic or inorganic halogen containing compound.

30 Typically the halogen compound is a halogen containing hydrocarbon. The hydrocarbon can have any number of carbon atoms, but for economic reasons under present economic conditions, typically less than about 20 carbon atoms per molecule.



Examples of the afore-mentioned compounds include, hexachloroethane, trichloroethane, tetrachloroethane, 1-bromobutane and diethylaluminiumchloride.

- 5 The use of said halogen compound is advantageous in catalyst system activity and reduces the quantity of undesirable by-product polymer.

The catalyst system may also contain a hydrocarbon compound as solvent for the homogeneous catalyst system. The hydrocarbon compound may be any  
10 saturated or unsaturated aliphatic hydrocarbon compound. The hydrocarbon compound can have any number of carbon compounds per molecule, but usually contain less than 20 carbon atoms due to commercial availability and end-use.

- 15 Typical unsaturated hydrocarbon compounds include, but are not limited to 1-hexene, 1,3-butadiene, 1,4-cyclo-octadiene, benzene, toluene, ethylbenzene, xylene, acetonitrile and the like. Further saturated hydrocarbon compounds include, but are not limited to cyclohexane, hexane, heptane, and the like.

Table 1

Run	Ligand	Cr(EH) <sub>3</sub> mmol	Molar Ratio Cr(EH) <sub>3</sub> :L: TEA:HCE	Temp (°C)	Press barg	Activity g prod/ g Cr/hr	Total Product g	Wt % Solid	Wt % Liquid	1-C6 in C-6 %	Liquid Product Distribution			
											Weight %			
											C-4	1-C6	C-6	C-8
1	1	2.2	0.0417	120	50	30300	33.7	1	99	80.3	2	73	18	0.5
2	1	2.2	0.0417	120	50	23100	25.8	1.5	98.5	80.4	2	71.5	17.5	1
3	1	2.2	0.0417	120	43	11000	12.3	2.5	97.5	79.5	3	71	18.5	1.5
4	1	2.2	0.0417	120	50	18800	20.7	0.5	99.5	80.7	2	70.5	17	1
5	1	1.1	0.0208	120	50	47800	26.6	0.5	99.5	80.4	1	74	18	0.5
6	1	1.1	0.0208	100	50	40700	22.5	0.5	99.5	82.3	0.5	76.5	16.5	0
7	1	1.1	0.0208	100	50	53300	29.4	0.5	99.5	82	0	75.5	16.5	0
8	1	2.2	0.0417	50	45	8600	11.6	18.5	81.5	86.5	3.5	68	11	1
9	1	2.2	0.0417	30	45	1700	6.7	72	28	83.5	4.5	50.5	10	4.5
10	1	1.1	0.0208	70	50	17900	10.1	3	97	85.1	4.5	75.5	13	0.5
11	1	1.1	0.0208	70	20	13500	7.5	1.5	98.5	82.2	0.5	72	15.5	0
12	1	2.2	0.0417	120	50	23500	26.2	1.5	98.5	80.6	3.5	75	18	0.5
13	1	2.2	0.0417	120	50	23500	26.2	1.5	98.5	80.8	5	73	17.5	0.5
14	2	4.3	0.0833	130	35	12300	27.8	5	95	56.8	1.5	40	30.5	2
15	3	2.2	0.0417	120	50	6300	10.7	14	86	65.5	6	55	28.5	2
16	4	4.3	0.0833	120	42	3000	8.2	20	80	61.6	5	36	22.5	2.5
17	5	2.2	0.0417	120	50	11800	14.1	8	92	68.3	2	54.5	25.5	1
18	6	4.3	0.0833	120	45	16800	37.3	3.5	96.5	73	0.5	67.5	25	0.5
19	7	1.1	0.0208	120	50	8400	4.8	3.5	95.5	79.6	2	66	17	1.5
20	8	1.1	0.0208	120	50	1700	1.1	18	82	73.5	7.5	53.5	19.5	7.5
21	9	1.1	0.0208	120	50	32000	17.6	0.5	99.5	82.1	2	76.5	16.5	0.5
22	9	1.1	0.0208	100	50	47000	26	0.5	99.5	83.4	0.5	77	15.5	0
23	9	1.1	0.0208	70	50	72000	40	1	99	85.7	0.5	75	12.5	0.5
24	10	1.1	0.0208	100	50	10000	5.7	2.5	97.5	81.7	2	69.5	15.5	0.5
25	11	1.1	0.0208	100	50	57700	31.8	0.5	99.5	83	0.5	77.5	16	0
26	11	1.1	0.0208	70	50	93500	52	1	99	85.2	0	74	13	0
27	12	1.1	0.0208	120	50	60600	33.6	0.5	99.5	76.8	1.5	70.5	21.5	0
28	12	1.1	0.0208	70	50	17100	9.7	3	97	80.7	0.5	70	17	0.5
29	13	1.1	0.0208	120	50	58300	32.2	0.5	99.5	78.9	1	73	19.5	0
30	13	1.1	0.0208	70	50	32200	17.9	1	99	81.2	0	74.5	17	0
31	14	1.1	0.0208	120	50	8300	4.7	3	97	62.9	1	60.5	35.5	0.5
32	14	1.1	0.0208	70	50	7200	4.2	4.5	95.5	68.9	1	66	29.5	0
33	15	1.1	0.0208	120	50	25600	15.1	7	93	55.4	1.5	43	34.5	1
34	16	4.3	0.0833	120	50	16000	35.2	2	98	61.3	1	48.5	30.5	1
35	17	2.2	0.0417	120	50	12400	13.3	2	98	68.7	2	61.5	25	1
36	18	2.2	0.0417	120	50	10700	11.6	2.5	97.5	75.4	3	67	22	1.5
37	19	2.2	0.0417	120	50	8500	10.6	12	88	77.6	5	66.5	19	1

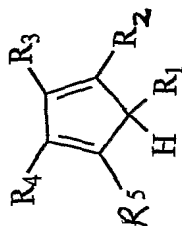


Table 2

<sup>†</sup> Ligand	Name	R1	R2	R3	R4	R5
1	1,2,3,4,5-pentaphenylcyclopenta-1,3-diene	Ph-	Ph-	Ph-	Ph-	Ph-
2	1,2,3,4-tetraphenylcyclopenta-1,3-diene	H-	Ph-	Ph-	Ph-	Ph-
3	1-phenyl-2,3,4,5-tetrapropylcyclopenta-1,3-diene	Pr-	Ph-	Pr-	Pr-	Pr-
4	1,4,5-triphenylcyclopenta-1,3-diene	Ph-	Ph-	H-	H-	Ph-
5	1,2,3,4-tetraphenyl-1,3-cyclopentadienyl-dimethyl- <i>t</i> -butylsilane	<i>t</i> -Bu(CH <sub>3</sub> ) <sub>2</sub> Si-	Ph-	Ph-	Ph-	Ph-
6	5-methyl-1,2,3,4-tetraphenylcyclopenta-1,3-diene	Me-	Ph-	Ph-	Ph-	Ph-
7	5-benzyl-1,2,3,4-tetraphenylcyclopenta-1,3-diene	Bz-	Ph-	Ph-	Ph-	Ph-
8	1,2,3,4,5-pentabenzylcyclopenta-1,3-diene	Bz-	Bz-	Bz-	Bz-	Bz-
9	1,2,3,4-tetraphenyl-5- <i>p</i> -tolylcyclopenta-1,3-diene	4-Me-Ph-	Ph-	Ph-	Ph-	Ph-
10	5-mesityl-1,2,3,4-tetraphenylcyclopenta-1,3-diene	Mesityl-	Ph-	Ph-	Ph-	Ph-
11	5-(4'- <i>t</i> -butylphenyl)-1,2,3,4-tetraphenylcyclopenta-1,3-diene	4- <i>t</i> Bu-Ph-	Ph-	Ph-	Ph-	Ph-
12	5-(4'-chlorophenyl)-1,2,3,4-tetraphenylcyclopenta-1,3-diene	4-Cl-Ph-	Ph-	Ph-	Ph-	Ph-
13	5-(4'-fluorophenyl)-1,2,3,4-tetraphenylcyclopenta-1,3-diene	4-F-Ph-	Ph-	Ph-	Ph-	Ph-
14	5-(pentafluorophenyl)-1,2,3,4-tetraphenylcyclopenta-1,3-diene	PentafluoroPh-	Ph-	Ph-	Ph-	Ph-
15	1,2,3,4-tetraphenyl-5-(phenylethynyl) cyclopenta-1,3-diene	Ph-C <sub>2</sub> -	Ph-	Ph-	Ph-	Ph-
16	2,3,4,5-tetraphenyl-2,4-cyclopentadienol	HO-	Ph-	Ph-	Ph-	Ph-
17	(1,3)(1,4)-di- <i>t</i> -butylcyclopenta-1,3-diene (mixture)	H-	<i>t</i> Bu-	H-	<i>t</i> Bu-*	<i>t</i> Bu-*
18	1,3-di- <i>t</i> -butyl-cyclopentadienyltrimethylsilane	(CH <sub>3</sub> ) <sub>3</sub> Si-	<i>t</i> Bu-	H-	<i>t</i> Bu-	H-
19	pentakis(4'- <i>t</i> -butylphenyl) cyclopenta-1,3-diene	4- <i>t</i> Bu-Ph-	4- <i>t</i> Bu-Ph-	4- <i>t</i> Bu-Ph-	4- <i>t</i> Bu-Ph-	4- <i>t</i> Bu-Ph-

<sup>†</sup> Some of the ligands used were mixtures of positional double bond isomers, however abstraction of the acidic proton with TEA, during catalyst preparation, gives a single delocalised carbanion that co-ordinates to the chromium centre.

\*Either/or

The invention is now described by way of non limiting examples.

The liquid product weight distribution for this and all other examples are given in **Table 1** and the structure and names of ligands used, are given in **Table 2**.

5

All procedures were carried out under inert conditions, using pre-dried reagents.

### Examples of performing the invention:

10

**Example 1:** Ethylene trimerisation using 1,2,3,4,5-pentaphenylcyclopenta-1,3-diene (**1**) as the ligand.

15

The catalyst system was prepared as follows: 0.0417 mmol of chromium(III) ethylhexanoate was combined with 0.125 mmol of 1,2,3,4,5-pentaphenylcyclopenta-1,3-diene, 0.21 mmol of hexachloroethane and stirred at room temperature for 30 minutes in 30 ml of dry cyclohexane. The catalyst complex was activated by adding 3.75 mmol of triethylaluminium at room temperature for a period of 2-5 min.

20

This solution, together with an additional 90 ml cyclohexane, was transferred to a pressure reactor, fitted with a mechanical stirrer. The reactor was charged with ethylene where after the reactor temperature was maintained at 120°C, while the ethylene pressure was kept at 50 barg. Thorough mixing was ensured by mixing speeds of 1100 RPM's. Thirty minutes later the reaction was terminated by the injection of 1-butanol/water into the pressure reactor. After releasing ethylene from the autoclave, the by product polymers in the reaction were separated by filtration and the product/solvent phase was analysed by GC.

30

A catalyst activity of 30 300 g product/g Cr/ hour was observed. The selectivity towards C<sub>6</sub> products was 91 mass%, while the selectivity observed towards 1-hexene formation was 73 mass %. The polymeric side product

obtained from the above reaction comprised 1 mass % of the reaction products.

**Example 2:** The procedure described in example 1 was followed except that  
5 90 ml cyclohexane and 10ml of 1-heptene, was charged to the pressure reactor.

**Example 3:** The procedure in example 1 was followed except that 1.4ml of  
2,6-di-*tert*-butylpyridine was also charged to the pressure reactor together  
10 with the 90 ml of cyclohexane, and the ethylene pressure was kept at 43 barg.

**Example 4:** The procedure in example 1 was followed except that 1.87 mmol of triethylaluminium was used to activate the catalyst.

15 **Example 5:** The procedure in example 1 was followed except that the catalyst system was prepared as follows: 0.0208 mmol of chromium(III) ethylhexanoate was combined with 0.0208 mmol of 1,2,3,4,5-pentaphenylcyclopenta-1,3-diene, 0.052 mmol of hexachloroethane and stirred at room temperature for 30 minutes in 30 ml of dry cyclohexane. The  
20 catalyst complex was activated by adding 0.468 mmol of triethylaluminium at room temperature for a period of 2-5 min.

**Example 6:** The procedure in example 5 was followed except that the  
25 reaction was conducted at 100°C.

**Example 7:** The procedure in example 5 was followed except that the pressure reactor was fitted with a gas entrainment stirrer and baffles and the reaction was conducted at 100°C.

30 **Example 8:** The procedure in example 1 was followed except that the reaction was conducted at 50°C and 45 barg.

**Example 9:** The procedure in example 8 was followed except that the reaction was conducted at 30°C.

**Example 10:** The procedure in example 5 was followed except that 0.94 mmol of triethylaluminium was used and the reaction was conducted at 70°C.

**Example 11:** The procedure in example 5 was followed except that 0.936 mmol of triethylaluminium was used, the reaction was conducted at 70°C and 20 barg.

**Example 12:** The procedure in example 1 was followed except that the catalyst system was prepared as follows: 0.0417 mmol of chromium(III) ethylhexanoate was combined with 0.0417 mmol of 1,2,3,4,5-pentaphenylcyclopenta-1,3-diene, 0.104 mmol of hexachloroethane and stirred at room temperature for 30 minutes in 30 ml of dry cyclohexane. The catalyst complex was activated by adding 2.30 mmol of triethylaluminium at room temperature for a period of 2-5 min and transferred to a pressure reactor. The reactor was first pressurised with H<sub>2</sub> to 1.5 barg and subsequently with ethylene to a pressure of 50 barg which was maintained throughout the reaction.

**Example 13:** The procedure in example 12 was followed except that the reactor was not pressurised with 1.5 barg H<sub>2</sub> before the addition of ethylene to the reactor.

**Example 14:** Ethylene trimerisation using 1,2,3,4-tetraphenylcyclopenta-1,3-diene (2) as the ligand. General workup conditions and stirring speeds from example 1 apply.

The catalyst system was prepared as follows: 0.0833 mmol of chromium(III) ethylhexanoate was combined with 0.25 mmol of 1,2,3,4-tetraphenylcyclopenta-1,3-diene and 0.42 mmol of hexachloroethane and stirred at room temperature for 30 minutes in 30 ml of dry cyclohexane. The

catalyst complex was activated by adding 3.75 mmol of triethylaluminium at room temperature for a period of 2-5 min.

This solution, together with an additional 90 ml cyclohexane, was charged to a pressure reactor. The reactor temperature was maintained at 130°C, while the ethylene pressure was kept at 35 barg.

**Example 15:** Ethylene trimerisation using 1-phenyl-2,3,4,5-tetrapropylcyclopenta-1,3-diene (**3**) as the ligand. General workup conditions and stirring speeds from example 1 apply.

The catalyst system was prepared as follows: 0.0417 mmol of chromium(III) ethylhexanoate was combined with 0.0417 mmol of 1-phenyl-2,3,4,5-tetrapropylcyclopenta-1,3-diene (**3**) and 0.10 mmol of hexachloroethane and stirred at room temperature for 30 minutes in 30 ml of dry cyclohexane. The catalyst complex was activated by adding 1.88 mmol of triethylaluminium at room temperature for a period of 2-5 min.

This solution, together with an additional 90 ml cyclohexane, was charged to a pressure reactor. The reactor temperature was maintained at 120°C, while the ethylene pressure was kept at 50 barg.

**Example 16:** Ethylene trimerisation using 1,4,5-triphenylcyclopenta-1,3-diene (**4**) as the ligand. General workup conditions and stirring speeds from example 1 apply.

The catalyst system was prepared as follows: 0.0833 mmol of chromium(III) ethylhexanoate was combined with 0.25 mmol of 1,4,5-triphenylcyclopenta-1,3-diene (**4**) and 0.42 mmol of hexachloroethane and stirred at room temperature for 30 minutes in 30 ml of dry cyclohexane. The catalyst complex was activated by adding 3.75 mmol of triethylaluminium at room temperature for a period of 2-5 min.

This solution, together with an additional 90 ml cyclohexane, was charged to a pressure reactor. The reactor temperature was maintained at 120°C, while the ethylene pressure was kept at 42 barg.

- 5    **Example 17:** Ethylene trimerisation using 1,2,3,4-tetraphenyl-1,3-cyclopentadienyl-dimethyl-*t*-butylsilane (**5**) as the ligand. General workup conditions and stirring speeds from example 1 apply.

10    The procedure in example 15 was followed except that the ligand was changed to 1,2,3,4-tetraphenyl-1,3-cyclopentadienyl-dimethyl-*t*-butylsilane (**5**).

**Example 18:** Ethylene trimerisation using 5-methyl-1,2,3,4-tetraphenylcyclopenta-1,3-diene (**6**) as the ligand. General workup conditions and stirring speeds from example 1 apply.

15

The procedure in example 16 was followed except that the ligand was changed to 5-methyl-1,2,3,4-tetraphenylcyclopenta-1,3-diene (**6**) and the reactor pressure was maintained at 45 barg.

- 20    **Example 19:** Ethylene trimerisation using 5-benzyl-1,2,3,4-tetraphenylcyclopenta-1,3-diene (**7**) as the ligand. General workup conditions and stirring speeds from example 1 apply.

25    The catalyst system was prepared as follows: 0.0208 mmol of chromium(III) ethylhexanoate was combined with 0.0208 mmol of 5-benzyl-1,2,3,4-tetraphenylcyclopenta-1,3-diene (**7**), 0.052 mmol of hexachloroethane and stirred at room temperature for 30 minutes in 30 ml of dry cyclohexane. The catalyst complex was activated by adding 0.94 mmol of triethylaluminium at room temperature for a period of 2-5 min.

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**Example 20:** Ethylene trimerisation using 1,2,3,4,5-pentabenzylcyclopenta-1,3-diene (**8**) as the ligand. General workup conditions and stirring speeds from example 1 apply.



The procedure in example 19 was followed except that the ligand was changed to 1,2,3,4,5-pentabenzylcyclopenta-1,3-diene (8).

**Example 21:** Ethylene trimerisation using 1,2,3,4-tetraphenyl-5-*p*-tolylcyclopenta-1,3-diene (9) as the ligand. General workup conditions and stirring speeds from example 1 apply.

The catalyst system was prepared as follows: 0.0208 mmol of chromium(III) ethylhexanoate was combined with 0.062 mmol of 1,2,3,4-tetraphenyl-5-*p*-tolylcyclopenta-1,3-diene (9), 0.052 mmol of hexachloroethane and stirred at room temperature for 30 minutes in 30 ml of dry cyclohexane. The catalyst complex was activated by adding 0.47 mmol of triethylaluminium at room temperature for a period of 2-5 min.

This solution, together with an additional 90 ml cyclohexane, was charged to a pressure reactor. The reactor temperature was maintained at 120°C, while the ethylene pressure was kept at 50 barg.

**Example 22:** The procedure in example 21 was followed except that the reaction was conducted at 100°C.

**Example 23:** The procedure in example 21 was followed except that 0.94 mmol of triethylaluminium was used and the reaction was conducted at 70°C.

**Example 24:** Ethylene trimerisation using 5-mesityl-1,2,3,4-tetraphenylcyclopenta-1,3-diene (10) as the ligand. General workup conditions and stirring speeds from example 1 apply.

The catalyst system was prepared as follows: 0.0208 mmol of chromium(III) ethylhexanoate was combined with 0.042 mmol of 5-mesityl-1,2,3,4-tetraphenylcyclopenta-1,3-diene (10), 0.052 mmol of hexachloroethane and stirred at room temperature for 30 minutes in 30 ml of dry cyclohexane. The catalyst complex was activated by adding 0.47 mmol of triethylaluminium at room temperature for a period of 2-5 min.

This solution, together with an additional 90 ml cyclohexane, was charged to a pressure reactor fitted with a gas entrainment stirrer and baffles. The reactor temperature was maintained at 100°C, while the ethylene pressure was kept at 50 barg.

**Example 25:** Ethylene trimerisation using 5-(4'-*t*-butylphenyl)-1,2,3,4-tetraphenylcyclopenta-1,3-diene (**11**) as the ligand. General workup conditions and stirring speeds from example 1 apply.

The catalyst system was prepared as follows: 0.0208 mmol of chromium(III) ethylhexanoate was combined with 0.062 mmol of 5-(4'-*t*-butylphenyl)-1,2,3,4-tetraphenylcyclopenta-1,3-diene (**11**), 0.052 mmol of hexachloroethane and stirred at room temperature for 30 minutes in 30 ml of dry cyclohexane. The catalyst complex was activated by adding 0.47 mmol of triethylaluminium at room temperature for a period of 2-5 min.

This solution, together with an additional 90 ml cyclohexane, was charged to a pressure reactor. The reactor temperature was maintained at 100°C, while the ethylene pressure was kept at 50 barg.

**Example 26:** The procedure in example 25 was followed except that 0.94 mmol of triethylaluminium was used and the reaction was conducted at 70°C.

**Example 27:** Ethylene trimerisation using 5-(4'-chlorophenyl)-1,2,3,4-tetraphenylcyclopenta-1,3-diene (**12**) as the ligand. General workup conditions and stirring speeds from example 1 apply.

The catalyst system was prepared as follows: 0.0208 mmol of chromium(III) ethylhexanoate was combined with 0.062 mmol of 5-(4'-chlorophenyl)-1,2,3,4-tetraphenylcyclopenta-1,3-diene (**12**), 0.052 mmol of hexachloroethane and stirred at room temperature for 30 minutes in 30 ml of dry cyclohexane. The catalyst complex was activated by adding 0.94 mmol of triethylaluminium at room temperature for a period of 2-5 min.

This solution, together with an additional 90 ml cyclohexane, was charged to a pressure reactor. The reactor temperature was maintained at 120°C, while the ethylene pressure was kept at 50 barg.

5

**Example 28:** The procedure in example 27 was followed except that the reaction was conducted at 70°C.

**Example 29:** The procedure in example 27 was followed except that the  
10 ligand was changed to 5-(4'-fluorophenyl)-1,2,3,4-tetraphenylcyclopenta-1,3-diene (**13**).

**Example 30:** The procedure in example 27 was followed except that the  
15 ligand was changed to 5-(4'-fluorophenyl)-1,2,3,4-tetraphenylcyclopenta-1,3-diene (**13**) and the reaction was conducted at 70°C.

**Example 31:** The procedure in example 27 was followed except that the  
20 ligand was changed to 5-(pentafluorophenyl)-1,2,3,4-tetraphenylcyclopenta-1,3-diene (**14**).

**Example 32:** The procedure in example 27 was followed except that the  
ligand was changed to 5-(pentafluorophenyl)-1,2,3,4-tetraphenylcyclopenta-1,3-diene (**14**) and the reaction was conducted at 70°C.

**Example 33:** The procedure in example 27 was followed except that the  
25 ligand was changed to 1,2,3,4-tetraphenyl-5-(phenylethynyl)-cyclopenta-1,3-diene (**15**).

**Example 34:** Ethylene trimerisation using 2,3,4,5-tetraphenyl-2,4-  
30 cyclopentadienol (**16**) as the ligand. General workup conditions and stirring speeds from example 1 apply.

The catalyst system was prepared as follows: 0.0833 mmol of chromium(III) ethylhexanoate was combined with 0.25 mmol of 2,3,4,5-tetraphenyl-2,4-

cyclopentadienol (**16**), 0.42 mmol of hexachloroethane and stirred at room temperature for 30 minutes in 30 ml of dry cyclohexane. The catalyst complex was activated by adding 3.75 mmol of triethylaluminium at room temperature for a period of 2-5 min.

5

This solution, together with an additional 90 ml cyclohexane, was charged to a pressure reactor. The reactor temperature was maintained at 120°C, while the ethylene pressure was kept at 50 barg.

10 **Example 35:** Ethylene trimerisation using a mixture of (1,3) and (1,4)-di-*t*-butylcyclopenta-1,3-diene (**17**) as the ligand. General workup conditions and stirring speeds from example 1 apply.

15 The catalyst system was prepared as follows: 0.0417 mmol of chromium(III) ethylhexanoate was combined with 0.125 mmol of (1,3)(1,4)-di-*t*-butylcyclopenta-1,3-diene (**17**), 0.21 mmol of hexachloroethane and stirred at room temperature for 30 minutes in 30 ml of dry cyclohexane. The catalyst complex was activated by adding 3.75 mmol of triethylaluminium at room temperature for a period of 2-5 min.

20

This solution, together with an additional 90 ml cyclohexane, was charged to a pressure reactor. The reactor temperature was maintained at 120°C, while the ethylene pressure was kept at 50 barg.

25 **Example 36:** The procedure in example 35 was followed except that the ligand was changed to 1,3-di-*t*-butyl-cyclopentadienyltrimethylsilane (**18**).

**Example 37:** Ethylene trimerisation using pentakis(4-*t*-butylphenyl)-cyclopenta-1,3-diene (**19**) as the ligand. General workup conditions and  
30 stirring speeds from example 1 apply.

The catalyst system was prepared as follows: 0.0417 mmol of chromium(III) ethylhexanoate was combined with 0.834 mmol of pentakis(4-*t*-butylphenyl)-cyclopenta-1,3-diene (**19**), 0.104 mmol of hexachloroethane and stirred at

room temperature for 30 minutes in 30 ml of dry cyclohexane. The catalyst complex was activated by adding 1.87 mmol of triethylaluminium at room temperature for a period of 2-5 min.

- 5 This solution, together with an additional 90 ml cyclohexane, was charged to a pressure reactor. The reactor temperature was maintained at 120°C, while the ethylene pressure was kept at 50 barg.

**Claims:**

1. A trimerisation catalyst system, which includes a chromium source and a ligand comprising a substituted five membered carbocyclic ring or derivatives thereof.

2. A catalyst system as claimed in claim 1, wherein the five membered carbocyclic ring is a substituted cyclopentadiene derivative of the general formula,  $C_5R_nH_{6-n}$ , wherein each R is a substituent and n is an integer from 1 to 5.

3. A catalyst system as claimed in claim 1 or claim 2, wherein the catalyst system is for the selective trimerisation of ethylene to 1-hexene.

4. A catalyst system as claimed in any one claims 1 to 3, which include, in combination with the ligand and the chromium source, one or more metal alkyls expressed by the following formulae:  $AlX_nR_{3-n}$  and  $R_nAlOR_{3-n}$ , wherein n is an integer from 0 - 3, X is a halogen atom, R is an alkyl group and the alkyl has less than about 20 carbon atoms per molecule.

5. A catalyst system as claimed in claim 4, which include a halogen source, which is selected from a group of compounds, which include hexachloroethane, trichloroethane, tetrachloroethane, 1-bromobutane and/ or diethylaluminiumchloride.

6. A catalyst system as claimed in any one of claims 1 to 5, wherein the chromium source is selected from a group including chromium(III)acetylacetonate, chromium (III) acetate, chromium (III) pyrrolides, chromium (III) 2,2,6,6-tetramethylheptadionate, chromium (III) tris(2-ethylhexanoate), bis(*N,N'*-bis(trimethylsilyl)benzamidinato) chromium (III) chloride, trichlorotris(4-isopropylpyridine) chromium (III), trichloro (*N,N,N',N',N''*-pentamethyldiethylenetriamine) chromium (III), chromium (III) chloride, bis-(2-dimethylphosphino-ethyl)ethylphosphine chromium (III), (2-dimethylphosphino-ethyl)(3-dimethylphosphinopropyl)methylphosphine

chromium (III) chromium (III) naphthenate, chromium (II) acetate, chromium (II) pyrrolides, chromium (II) bis(2-ethylhexanoate) and/or chromium (II) chloride.

- 5 7. A catalyst system as claimed in any one of claims 2 to 6, wherein the substituents, R, are independently selected from the group which includes alkyl, aryl, arylalkyl, aryloxy, halogen, nitro, alkoxycarbonyl, carbonyloxy, alkoxy, silyl, aminocarbonyl, carbonylamino, dialkylamino, and/ or derivatives thereof, and/ or aryl substituted with any of these substituents.

10

8. A catalyst system as claimed in claim 7, wherein the aryl or arylalkyl group is selected from a phenyl, benzyl, tolyl, *t*-butylphenyl, chlorophenyl, fluorophenyl or pentafluorophenyl group.

- 15 9. A catalyst system as claimed in claim 2, wherein n is 5 and the aryl group a phenyl.

10. A catalyst system as claimed in claim 1 or 2, wherein the ligand is selected from the group which includes 1,2,3,4-tetraphenylcyclopenta-1,3-  
 20 diene, 1,2,3,4,5-pentaphenylcyclopenta-1,3-diene, 1,2,3,4,5-pentabenzylcyclopenta-1,3-diene, 5-methyl-1,2,3,4-tetraphenylcyclopenta-1,3-diene, 1,3-diphenylcyclopenta-1,3-diene, 1-phenyl-2,3,4,5-tetrapropylcyclopenta-1,3-diene, 1,4,5-triphenylcyclopenta-1,3-diene, 1,2,3,4-tetraphenyl-1,3-cyclopentadienyl-dimethyl-*t*-butylsilane, 5-benzyl-1,2,3,4-  
 25 tetraphenylcyclopenta-1,3-diene, 1,2,3,4-tetraphenyl-5-*p*-tolylcyclopenta-1,3-diene, 5-mesityl-1,2,3,4-tetraphenylcyclopenta-1,3-diene, 5-(4'-*t*-butylphenyl)-1,2,3,4-tetraphenylcyclopenta-1,3-diene, 5-(4'-chlorophenyl)-1,2,3,4-tetraphenylcyclopenta-1,3-diene, 5-(4'-fluorophenyl)-1,2,3,4-tetraphenylcyclopenta-1,3-diene, 5-(pentafluorophenyl)-1,2,3,4-  
 30 tetraphenylcyclopenta-1,3-diene, 1,2,3,4-tetraphenyl-5-(phenylethynyl)cyclopenta-1,3-diene, 2,3,4,5-tetraphenyl-2,4-cyclopentadienol, (1,3)(1,4)-di-*t*-butylcyclopenta-1,3-diene, 1,3-di-*t*-butyl-cyclopentadienyltrimethylsilane, pentakis(4'-*t*-butylphenyl) cyclopenta-1,3-diene and/ or derivatives thereof.

11. A catalyst system as claimed in any one of claims 4 to 10, wherein the metal alkyl is selected from a group of compounds which include alkyl aluminium compounds, hydrolyzed alkyl aluminium compounds (aluminoxanes), alkyl boron compounds, alkyl magnesium compounds, alkyl zinc compounds and/or alkyl lithium compounds.

12. A catalyst system as claimed in claim 11, wherein the metal alkyl is selected from a group of alkyl aluminium compounds which include trimethyl aluminium, triethyl aluminium, tripropyl aluminium, tributyl aluminium, triisobutyl aluminium, diethyl aluminium chloride, diethyl aluminium bromide, diethyl aluminium ethoxide, ethyl aluminium dichloride, ethyl aluminium sesquichloride, and mixtures thereof.

13. A catalyst system as claimed in any one of claims 1 to 12, wherein the catalyst system is a homogeneous catalyst system, which includes a hydrocarbon compound as solvent for the homogeneous catalyst system.

14. A catalyst system as claimed in claim 13, wherein the hydrocarbon compound as the solvent is an unsaturated hydrocarbon compound, which is selected from a group, which includes 1-hexene, 1,3-butadiene, 1,4-cyclo-octadiene, benzene, toluene, ethylbenzene, xylene and/ or acetonitrile.

15. A catalyst system as claimed in claim 13, wherein the hydrocarbon compound as the solvent is a saturated hydrocarbon compound, which is selected from a group, which includes cyclohexane, hexane and/ or heptane.

16. A process for producing 1-hexene in a high selectivity and yield by the trimerisation of ethylene under trimerisation conditions of a temperature ranging between 25 °C and 150 °C and a pressure ranging between 5 and 80 barg, in the presence of an ethylene trimerisation catalyst system which includes a chromium source and a ligand comprising a substituted five membered carbocyclic ring or derivatives thereof.



17. A process as claimed in claim 16, wherein the carbocyclic ring ligand is a substituted cyclopentadiene, which is either affirmatively added to the catalyst system, to the reaction mixture, or generated in-situ.

5

18. A process as claimed in claim 17, wherein the ligand is formed or generated by the compounds selected from a group, which includes 1,2,3,4,5-pentaphenylcyclopentadiene, lithium 1,2,3,4,5-pentaphenylcyclopentadienide, diethyl-aluminium-1,2,3,4,5-pentaphenylcyclopentadienide, 1,3-diphenylcyclopentadiene, lithium 1,3-diphenylcyclopentadienide, diethylaluminium-1,3-diphenylcyclopentadienide, 1,2,3,4-tetraphenylcyclopentadiene, lithium 1,2,3,4-tetraphenylcyclopentadienide, diethyl-aluminium-1,2,3,4-tetraphenylcyclopentadienide or the like.

19. A ligand for a trimerisation catalyst system which includes a chromium source, the ligand comprising a substituted five membered carbocyclic ring or derivatives thereof.

20. A ligand as claimed in claim 19, wherein the catalyst system is for the substantially selective trimerisation of ethylene to 1-hexene.

21. A ligand as claimed in claim 19 or claim 20, wherein the ligand is a substituted cyclopentadiene derivative of the general formula,  $C_5R_nH_{6-n}$ , wherein each R is a substituent and n is an integer from 1 to 5.

25

22. A ligand as claimed in claim 21, wherein the substituents, R, are independently selected from the group, which includes alkyl, aryl, arylalkyl, aryloxy, halogen, nitro, alkoxycarbonyl, carbonyloxy, alkoxy, silyl, aminocarbonyl, carbonylamino, dialkylamino, or derivatives thereof, or aryl substituted with any of these substituents.

30

23. A ligand as claimed in claim 22, wherein the aryl or arylalkyl group is selected from a phenyl, benzyl, tolyl, *t*-butylphenyl, chlorophenyl, fluorophenyl or pentafluorophenyl group.

24. A ligand as claimed in claim 23, wherein n is 5 and the aryl group a phenyl.

5 25. A ligand as claimed in claim 22, wherein the silyl group is selected from a dimethyl-*t*-butylsilane or trimethylsilane group.

26. A ligand as claimed in claim 22, wherein the ligand is selected from the group which includes 1,2,3,4-tetraphenylcyclopenta-1,3-diene, 1,2,3,4,5-pentaphenylcyclopenta-1,3-diene, 1,2,3,4,5-pentabenzylcyclopenta-1,3-diene, 5-methyl-1,2,3,4-tetraphenylcyclopenta-1,3-diene, 1,3-diphenylcyclopenta-1,3-diene, 1-phenyl-2,3,4,5-tetrapropylcyclopenta-1,3-diene, 1,4,5-triphenylcyclopenta-1,3-diene, 1,2,3,4-tetraphenyl-1,3-cyclopentadienyl-dimethyl-*t*-butylsilane, 5-benzyl-1,2,3,4-tetraphenylcyclopenta-1,3-diene, 1,2,3,4-tetraphenyl-5-*p*-tolylcyclopenta-1,3-diene, 5-mesityl-1,2,3,4-tetraphenylcyclopenta-1,3-diene, 5-(4'-*t*-butylphenyl)-1,2,3,4-tetraphenylcyclopenta-1,3-diene, 5-(4'-chlorophenyl)-1,2,3,4-tetraphenylcyclopenta-1,3-diene, 5-(4'-fluorophenyl)-1,2,3,4-tetraphenylcyclopenta-1,3-diene, 5-(pentafluorophenyl)-1,2,3,4-tetraphenylcyclopenta-1,3-diene, 1,2,3,4-tetraphenyl-5-(phenylethynyl)cyclopenta-1,3-diene, 2,3,4,5-tetraphenyl-2,4-cyclopentadienol, (1,3)(1,4)-di-*t*-butylcyclopenta-1,3-diene (mixture), 1,3-di-*t*-butylcyclopentadienyltrimethylsilane, pentakis(4'-*t*-butylphenyl) cyclopenta-1,3-diene and/ or derivatives thereof.

25

27. A trimerisation catalyst system substantially as described herein.

28. A process for producing 1-hexene substantially as described herein.

30 29. A ligand for a trimerisation catalyst system substantially as described herein.